

CLAIMS

We Claim:

1. A process for the preparation of dialkyl carbonate comprising:

reacting carbon monoxide, at least one alkanol and an oxygen-containing gas in the presence of a ionic halogen free copper catalyst, thereby forming said dialkyl carbonate in a crude dialkyl carbonate product.

2. The process of claim 1, wherein said catalyst is selected from the group consisting of: [1,1'(1-butylbenzimidazol-2yl)pentane]copper(II) di(trifluoromethanesulfonate), [1,1'bis(1-ethylbenzimidazol-2yl)propane]copper(II) di(tosylate), *rac*-[2,2'-bis[2-(1-ethylbenzimidazol-2yl)biphenyl]copper(II) di(trifluoroacetate), *rac*-[[*S*-2,2'-bis[2-(1-butyylimidazol-2yl)biphenyl]copper(II) di(pentafluorobenzoate, and *rac*-[[*S*-2,2'-bis[2-(1-octylbenzimidazol-2yl)biphenyl]copper(II) di(pentafluorophenylsulfonate).

3. The process of claim 1, wherein the molar ratio of said carbon monoxide to said oxygen-containing gas is between about 3:1 to about 100:1.

4. The process of claim 1, wherein said reaction step is carried out at a temperature between about 40 °C to about 200 °C and at a pressure between about atmospheric pressure up to about 1400 Mpa.

5. The process of claim 1, wherein said catalyst is present from about 10 g/l to 300 g/l of the total reaction mixture.

6. The process of claim 1, further comprising recovering a dialkyl carbonate enriched stream from said crude dialkyl carbonate product.

7. The process of claim 6, wherein said recovery step is at least one step selected from the group consisting of distillation, filtration, decanting, centrifugation, demixing, absorption on solid absorbents and permeation through selective membranes.

8. The process of claim 1, wherein said alkanol is methanol and said dialkyl carbonate is dimethyl carbonate.

9. The process of claim 8, wherein said alkanol is present in a concentration from about 30 wt% to about 95 wt% of the total reaction mixture.

10. The process of claim 8, further comprising water in a concentration from about 1 wt% to about 10 wt% of the total reaction mixture. 11. The process of claim 1, further comprising an inert gas.

11. The process of claim 11, wherein said inert gas is selected from the group consisting of nitrogen, argon and a mixture thereof.

12. The process of claim 1, wherein said catalyst is a homogeneous catalyst.

13. The process of claim 1, wherein said catalyst is a heterogeneous catalyst.

14. The process of claim 1, wherein said catalyst comprises a support.

15. The process of claim 15, wherein said support comprises at least one material selected from the group consisting of alumina, silica, and a polymeric material.

16. The process of claim 1, wherein said process is a continuous process.

17. The process of claim 1, wherein said process is a batch process.

18. A composition useful for the preparation of dialkyl carbonates, the composition comprising:

an ionic halogen free catalyst;

carbon monoxide;

an alkanol; and

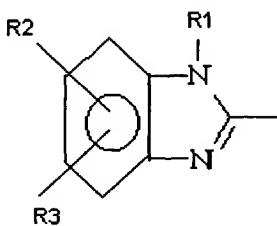
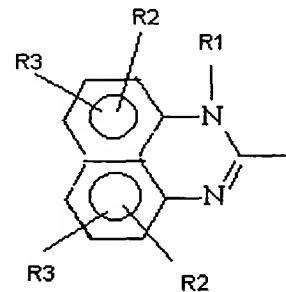
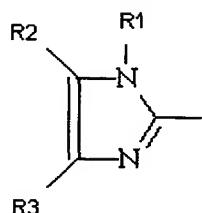
an oxygen-containing gas.

19. The composition of claim 1, wherein the ionic halogen free catalyst has the formula LM X₁ X₂, wherein X₁ and X₂ are independently selected from the group consisting of hydride, triflate, acetate, trifluoroacetate, perfluorotetraphenyl borate, tetrafluoro borate, C₁ through C₁₂ straight chain or branched alkyl or alkoxy, C₃ through C₁₂ cycloalkyl or cycloalkoxy, and aryl, wherein M is selected from the group consisting of Cu, Ag, and Au; and wherein L comprises a nitrogen-containing bidentate ligand with more than 2 nitrogen atoms.

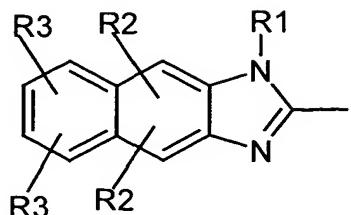
20. The composition of claim 21, wherein L comprises a nitrogen-containing bidentate ligand represented by the formula:

[AZA'] and [AA'],

wherein A and A' are independently selected from the group consisting of



, and



wherein R₁ is independently selected from the group consisting of hydrogen, C₁ through C₁₂ straight chain or branched alkyl, C₃ through C₁₂ cycloalkyl, aryl, and trifluoroethane; R₂ and R₃ are independently selected from the group consisting of hydrogen, C₁ through C₁₂ straight chain or branched alkyl, C₃ through C₁₂ cycloalkyl, C₁ through C₁₂ alkoxy, F, Cl, SO₃, C₁ through C₁₂ perfluoroalkyl, and N(CH₃)₂; wherein Z is selected from the group consisting of non-substituted C₁, through C₁₂ alkyl, C₃ through C₁₂ cycloalkyl; methoxy; amino; halo; C₁, through C₁₂ haloalkyl substituted alkyl, cycloalkyl of up to 12 carbon atoms, C₁-C₄₀ aryl; and C₁-C₄₀ alkylaryl; and wherein X₁ and X₂ are independently selected from the group consisting of hydride, triflate, acetate, trifluoroacetate, perfluorotetraphenylborate, tetrafluoroborate, C₁, through C₁₂ alkyl, C₁, through C₁₂ alkoxy, C₃ through C₁₂ cycloalkyl, C₃ through C₁₂ cycloalkoxy, and aryl.